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ABSTRACT

In protostellar cores where the dust temperature has been raised above 100K and subsequently allowed to fall below the condensation temperature of methanol, *recondensation* on to cooling grains removes methanol molecules from the gas at rates faster (~ 1000 times) than those of chemical reactions. Molecular recondensation can have a profound effect on the chemical composition of hot cores. The methanol chemistry of hot cores is solved analytically and the trend in molecule binding energies required is compared with theoretical and experimental values.

It is demonstrated, through a model calculation incorporating recondensation, that it yields a consistent explanation of the similarity of the CH_3OH , CH_3OCH_3 and HCOOCH_3 abundances measured in G34.3 and W3(H_2O) by Macdonald et al. (1996) and by Helmich & van Dishoeck (1997). These observations suggest that the latter molecules could not be derived from CH_3OH through gas phase reactions. The manner in which molecular recondensation could affect the interpretation of hot core chemistry in general, particularly of organic molecules, is briefly discussed.

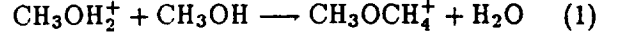
Subject headings: ISM: clouds - ISM: abundances - ISM: molecules - molecular processes

1. Introduction

In the energetic environments of forming massive and low-mass protostars, thermal heating or sputtering in shock waves can liberate the molecular ice mantles that cover interstellar dust grains (e.g. Blake et al. 1987; van Dishoeck et al. 1993). Observations of these hot cores can therefore be used to probe the nature of grain surface chemistry. The desorbed molecules can themselves initiate distinctive gas phase reaction pathways leading to the growth of highly complex organic molecules (Charnley et al. 1995), oxygen-nitrogen molecular differentiation (Charnley et al. 1992; Caselli et al. 1993), and the possibility of comparing dynamical timescales through ‘molecular clocks’ (Charnley 1997a; Hatchell et al. 1998). One success of this scenario is the explanation, based on reactions originally proposed by Blake et al., of the high observed abundances of dimethyl ether (CH_3OCH_3) and methyl formate (HCOOCH_3) as being due to protonation of methanol molecules evaporated from grain surfaces followed by methyl cation transfer reactions with methanol and formaldehyde leading, following electron dissociative recombinations, to CH_3OCH_3 and HCOOCH_3 respectively.

Recent line surveys of star-forming regions have, however, raised problems for the standard theory of hot core chemistry (Brown et al. 1988; Charnley et al. 1992). Observations of the G34.3 and W3(H_2O) cores indicate that the CH_3OH abundances are lower than in other cores and comparable with those of its putative daughter molecules (Macdonald et al. 1996; Helmich & van Dishoeck 1997). Table 1 summarises the relevant observational data. As models predict that at most a few per cent of the evaporated methanol is converted to CH_3OCH_3 and HCOOCH_3 (Charnley et al. 1992), it would be difficult to reproduce the CH_3OCH_3 abundance in G34.3 even with the higher CH_3OH abundance determined by Mehringer & Snyder (1996). It has therefore been suggested that they cannot be formed by gas phase reactions, as previously thought, but that they are, like methanol, the products of grain surface reactions.

While the proposed gas phase synthesis of HCOOCH_3 is not supported by methyl cation transfer experiments (see Karpas & Mautner 1989), and in fact may involve HCOOH instead of H_2CO (Charnley 1999a), the situation is much more serious for the currently accepted origin of CH_3OCH_3 . The reaction



is well-studied in the laboratory with a measured rate coefficient (Karpas & Mautner 1989) and its inclusion in models of methanol-rich hot cores reproduces the $\text{CH}_3\text{OCH}_3/\text{CH}_3\text{OH}$ abundance ratios typically observed in many sources (Charnley et al. 1992; Caselli et al. 1993). It is therefore puzzling that this theory should be at variance with the observational data for the G34.3 and W3(H_2O) cores. There is apparently insufficient CH_3OH to produce the CH_3OCH_3 and HCOOCH_3 by ion-molecule chemistry, suggesting that the standard theory is in need of revision and perhaps indicating a mantle origin for these molecules.

A key assumption of all previous hot core models has been that once the dust grain temperature, T_d , is raised above the condensation temperature of water, and the entire mantles evaporated, the grains remain hot, with $T_d > 100\text{K}$, for the nominal ‘age’ of the core, estimated to be $\sim 10^5$ years (e.g. Walmsley 1989). Theoretically, the gas and dust in hot cores should be thermally well-coupled with $T \sim T_d \sim 100 - 300\text{K}$; observations by Schilke et al. (1992) show that this is indeed the case in Orion-KL. In these dense regions ($n_H \sim 10^6 - 10^8 \text{cm}^{-3}$), the gas-grain collision rates for neutral molecules X , $\lambda(X)$, are high. However the associated thermal desorption rates, $\xi(X)$, are very large for T_d above 100K since they have an exponential dependence on T_d

$$\xi(X) = \nu_X \exp\left[-\frac{E_X}{kT_d}\right] \quad (2)$$

where ν_X is the vibrational frequency of X in a surface binding site, typically $10^{12} - 10^{13} \text{s}^{-1}$, k is the Boltzmann constant, and E_X is the binding (or adsorption) energy for physisorption (e.g. Sandford & Allamandola 1993). This is the reason why hot core chemistry is highly transient and requires a time-dependent treatment. For cooler cores with T_d below about 40K, the $\xi(X)$ for the most abundant volatiles (i.e. $X = \text{CO}, \text{O}_2, \text{N}_2$) are sufficiently low that a gas-grain chemical steady-state can occur (Charnley 1997b). Hence, in a core where the dust has been raised above 100K and subsequently allowed to cool, molecule X will condense back on to the cooling grains when T_d falls below its condensation temperature.

In this paper I consider the effect of *molecular recondensation* on hot core chemistry. I describe

the relevant gas phase chemistry of CH_3OH and CH_3OCH_3 semi-analytically and show that although methanol molecules can be removed from the gas at rates comparable to, or in excess of (~ 1000 times), those of chemical reactions, CH_3OCH_3 molecules can still be present in the gas. The detection of solid HCOOH by the Infrared Space Observatory (Schutte et al. 1996) at about 1% of H_2O would correspond to a gas phase abundance upon evaporation of $\sim 10^{-7}$. However, this is in conflict with gas phase HCOOH abundances actually observed in star-forming regions ($\sim 10^{-10} - 10^{-9}$) and so I also explore whether recondensation of HCOOH could resolve this issue.

2. Methanol and Dimethyl Ether in Hot Cores

In this section I first present the relevant details of the methanol (MeOH) and dimethyl ether (Me_2O) gas phase chemistries, showing quantitatively how the $\text{Me}_2\text{O}/\text{MeOH}$ ratio could be affected by recondensation. Once evaporated, methanol is protonated by H_3O^+ , HCO^+ and H_3^+ but is reformed by dissociative recombination with electrons. It is removed primarily through reaction (1) and by He^+ and C^+ . Utilising the reaction rate coefficients compiled by Millar et al. (1997a), the $\text{MeOH}-\text{Me}_2\text{O}$ gas phase chemistry obeys the following differential equations for the fractional abundances $y(X) = n(X)/n_{\text{H}}$ (with $n(X)$ the number density of X)

$$\begin{aligned} n_{\text{H}}^{-1} \dot{y}(\text{MeOH}) = & 300T_3^{-0.5} x_e y(\text{MeOH}_2^+) \\ & - 0.076T_3^{-1.6} y(\text{MeOH}) y(\text{MeOH}_2^+) \\ & + [2.5y(\text{H}_3\text{O}^+) + 2.7y(\text{HCO}^+) + 5.7y(\text{H}_3^+) \\ & + 2.2y(\text{He}^+) + 7.3y(\text{C}^+)] y(\text{MeOH}) \end{aligned} \quad (3)$$

$$\begin{aligned} n_{\text{H}}^{-1} \dot{y}(\text{Me}_2\text{O}) = & 150T_3^{-1.6} x_e y(\text{Me}_2\text{OH}^+) \\ & - \{[2.7y(\text{H}_3\text{O}^+) + 2.1y(\text{HCO}^+) + 2.0y(\text{H}_3^+)] \\ & + 2[y(\text{H}^+) + y(\text{He}^+) + y(\text{C}^+)]\} y(\text{Me}_2\text{O}) \end{aligned} \quad (4)$$

where $\dot{y}(X) = dy(X)/dt_9$, and $dt_9 = 10^{-9} dt$. The electron fraction has been written distinctly as x_e and $T_3 = T/300\text{K}$. After about one year post-evaporation the gas ionization is in a steady-state to a good approximation. When no metals (e.g. Na, Mg, Fe) are evaporated the electron fraction is given by

$$x_e \approx y(\text{MeOH}_2^+) + y(\text{HCO}^+) + y(\text{H}_3\text{O}^+) + y(\text{H}_3^+)$$

and is constant for the age of the core. The distribution of positive charge is determined by a proton transfer cascade from H_2 to CO to H_2O , terminating at MeOH when $\text{NH}_3/\text{MeOH} \ll 1$. As H_2O and MeOH are removed, HCO^+ becomes the major ion at longer times (cf. Charnley et al. 1992, 1995). The loss of protonated methanol is governed by ion-molecule reactions rather than grain collisions and its steady-state abundance can be expressed as

$$\frac{y(\text{MeOH}_2^+)}{y(\text{MeOH})} = \frac{2.5y(\text{H}_3\text{O}^+) + 2.7y(\text{HCO}^+) + 5.7y(\text{H}_3^+)}{300T_3^{-0.5} x_e + 0.076T_3^{-1.6} y(\text{MeOH})} \quad (5)$$

Substituting equation (5) in equation (3), we can write the differential equation for the methanol abundance due solely to gas phase chemistry, it is

$$\dot{y}(\text{MeOH}) = \left(\left[\frac{a - y(\text{MeOH})}{a + y(\text{MeOH})} - 1 \right] b - c \right) y(\text{MeOH}) \quad (6)$$

where

$$\begin{aligned} a &= 3.95 \times 10^3 T_3^{1.1} x_e \\ b &= n_{\text{H}} [2.5y(\text{H}_3\text{O}^+) + 2.7y(\text{HCO}^+) + 3.1y(\text{H}_3^+)] \\ c &= n_{\text{H}} [2.6y(\text{H}_3^+) + 2.2y(\text{He}^+) + 7.3y(\text{C}^+)] \end{aligned}$$

The appearance of $y(\text{H}_3^+)$ in both b and c is because H_3^+ protonates MeOH both dissociatively and nondissociatively. For standard values of the cosmic ray ionization rate, $\zeta \sim 10^{-17} \text{ s}^{-1}$ and a core density of $n_{\text{H}} \sim 10^7 \text{ cm}^{-3}$, the electron fraction is $x_e \sim 10^{-9}$ (Charnley et al. 1995) and so at 200K, $a \sim 2.5 \times 10^{-6}$. The maximum values of $y(\text{MeOH})$ obtained from both gas phase and solid phase observations are around 5×10^{-7} (Menten et al. 1988; Schutte 1996) and so equation (6) has the solution $y(\text{MeOH}) \propto \exp[-(\frac{1}{3}b + c)t_9]$ early in the evolution, and the solution $y(\text{MeOH}) \propto \exp[-ct_9]$ at longer times when $a \gg y(\text{MeOH})$.

We now consider the effect of the gas-grain interaction. The collision rate of methanol molecules with the dust grains is

$$\lambda(\text{MeOH}) = 4.55 \times 10^{-18} \left(\frac{T}{M_{\text{MeOH}}} \right)^{0.5} n_{\text{H}} \quad (7)$$

where M_{MeOH} is the molecular weight. In writing equation (7), unit sticking efficiency on $0.1 \mu\text{m}$ grains

and a dust number density of $10^{-12}n_H$ have been assumed. Using the same scaling as for the chemical rate coefficients in equations (3) and (4), one has

$$\lambda_9(\text{MeOH}) = 1.4 \times 10^{-8} T_3^{0.5} n_H \quad (8)$$

The relative importance for methanol loss through chemical reactions as opposed to sticking collisions with dust grains is given by the ratio

$$\frac{c}{\lambda_9(\text{MeOH})} = \frac{2.6y(\text{H}_3^+) + 2.2y(\text{He}^+) + 7.3y(\text{C}^+)}{1.4 \times 10^{-8} T_3^{0.5}} \quad (9)$$

Noting that, for these ions, loss in gas phase reactions dominates that by grain collisions, we can evaluate equation (9) using analytical formulae derived from Charnley (1997b).

$$n(\text{He}^+) = \frac{0.5\zeta_9 y(\text{He})}{1.6y(\text{CO}) + 1.8 \times 10^{-5} \exp(-35/T)} \quad (10)$$

$$n(\text{C}^+) \approx \frac{1.6y(\text{He}^+)n(\text{CO})}{2.0y(\text{H}_2\text{O})} \quad (11)$$

$$n(\text{H}_3^+) \approx \frac{0.5\zeta_9}{1.7y(\text{CO})} \quad (12)$$

where ζ_9 is $10^9\zeta$. Adopting a core density of $n_H = 2 \times 10^7 \text{cm}^{-3}$, $T=200\text{K}$, $\zeta_9 = 10^{-8}\text{s}^{-1}$, $y(\text{CO}) = 10^{-4}$, $y(\text{He}) = 0.1$ and $y(\text{H}_2\text{O}) = 10^{-5}$, one finds that $c/\lambda_9(\text{MeOH}) \approx 6 \times 10^{-4}$. Hence, if the dust grains are at a temperature below the condensation temperature of methanol, almost all colliding methanol molecules are retained on the grain surfaces - *recondensation* of MeOH dominates the removal of methanol over that due to chemical reactions. This adds a term $-n_H^{-1}\lambda_9(\text{MeOH})y(\text{MeOH})$ to the right-hand side of each of equations (3) and (4). The solution of equation (6) becomes $y(\text{MeOH}) \propto \exp[-(c + \lambda_9)t_9] \approx \exp[-\lambda t]$

What effect will MeOH recondensation have on the evolution of its daughter molecules? If the binding energy of MeOH on dust is much greater than that of Me_2O and the grains are sufficiently warm that Me_2O does not recondense, we can answer this question by considering the Me_2O differential equation (4). The production of Me_2O is intimately connected to the abundance of MeOH through equation (5); it is also destroyed by the low-abundance ions H^+ , He^+ and C^+ but, unlike MeOH, Me_2O is only produced in half of the electron dissociative recombinations of the protonated form, Me_2OH^+ . Now, suppose that the core

chemistry has evolved to some post-evaporation time t such that an appreciable abundance of Me_2O has been formed via reaction (1) and the methanol abundance is still close to that originally injected. If all the methanol molecules were to be instantaneously removed, the Me_2O abundance in the gas would not be affected instantaneously, but instead Me_2O molecules would be removed after τ seconds where

$$\tau = \frac{10^9}{n_H} \{2.7y(\text{H}_3\text{O}^+) + 2.1y(\text{HCO}^+) + 2.0y(\text{H}_3^+) + 2[y(\text{H}^+) + y(\text{He}^+) + y(\text{C}^+)]\}^{-1} \quad (13)$$

When methanol is absent, H_3O^+ is the dominant ion, $y(\text{H}_3\text{O}^+) \approx x_e \approx 10^{-9}$, and so, for a core density of $n_H \sim 10^7 \text{cm}^{-3}$, one finds $\tau(\text{Me}_2\text{O}) \approx 10^3$ years. Hence, there should exist values of T_d and t for which, as the grains cool, MeOH is selectively recondensed but the MeOH already incorporated into Me_2O can remain in the gas at a reasonably high abundance, until eventually it too is removed, either by recondensation, if the grains cool sufficiently rapidly, or by chemical reactions.

3. Dust Temperature Fluctuations Around Massive Protostars

Molecular recondensation, as outlined above, clearly requires time variation in the local dust grain temperature within a hot core. Grains must be heated sufficiently to desorb H_2O , CH_3OH , and also HCOOH , then be allowed to cool to about 90-100K. Luminosity variations, $L_*(t)$, of the central protostar offer the simplest means of realising this. A dust grain located a distance r from the protostar, where the emission is optically thin, will have a temperature (e.g. Emerson 1988)

$$T_d(r, t) \propto L_*^{1/4}(t) r^{-2/5} \quad (14)$$

where the flux-averaged emissivity is assumed to have a ν^1 frequency dependence. The luminosity of a massive protostar can be written as (cf. Stahler, Palla & Ho 1999)

$$L_*(t) = \frac{GM_*}{R_*} \dot{M}(t) + L_{\text{int}} \quad (15)$$

where M_* and R_* are the protostellar mass and radius, $\dot{M}(t)$ is the mass accretion rate and L_{int} is

the intrinsic luminosity due to protostellar contraction at the end of the convective phase. As $L_{\text{int}} \propto M_*^{11/2} R_*^{-1/2}$, this term comes to dominate $L_*(t)$ as the mass of the protostar increases. However, during the earliest phases of formation, when M_* is small, $L_*(t)$ is set mostly by the accretion luminosity. Temporal variations in $\dot{M}(t)$ could therefore potentially have the most pronounced effect on $L_*(t)$, and hence on $T_d(r, t)$. Mass accretion must start to diminish at some point. Stahler et al. (1999) suggested that $\dot{M}(t)$ may decay rapidly relative to changes (i.e. growth) in L_{int} . The mechanism responsible for the ultimate cessation in $\dot{M}(t)$ is uncertain but could be linked to the presence of outflows or to magnetic support of the parent cloud core (see Stahler et al. 1999).

One may therefore speculate that, as a massive protostar begins to form, sporadic variations in $\dot{M}(t)$ could occur throughout the earliest phases of hot core evolution, mediated by the same processes that ultimately terminate mass accretion. A more detailed discussion of this point is beyond the scope of this paper, however, we note that, although having different physical origin, strong variations in both $\dot{M}(t)$ and $L_*(t)$ are known to be important in the earliest phases of low-mass star formation - the FU Orionis phenomenon (Hartmann et al. 1993). As massive protostars spend much of their youth still embedded in their natal core, small fluctuations in their luminosity are much more difficult to discern. As only a lowering of T_d by a few kelvin may be sufficient to permit recondensation, only a modest reduction in $\dot{M}(t)$ is necessary. For example, a reduction in $\dot{M}(t)$ by about a factor of 5 will lower $T_d(r, t)$ by a factor of 1.5.

4. Surface Binding (Adsorption) Energies

We now address the question of what absolute and relative E_X values for each of these four molecules will make the recondensation scenario tenable, how consistent these are with known experimental or theoretical values, and the associated implications for the surface structure of interstellar grains. We adopt the convention of expressing binding energies in temperature units.

The preceding analysis considered only gas phase chemistry and, as methanol removal cannot occur instantaneously in practice, one must consider molecular desorption from grains. The methanol gas-grain chemistry is governed by the coupled differential

equations

$$\begin{aligned} \dot{y}(\text{MeOH}) &= n_{\text{H}} G(\text{MeOH}) - \lambda_9(\text{MeOH}) y(\text{MeOH}) \\ &+ \nu_9 \exp\left[-\frac{E_{\text{MeOH}}}{kT_d}\right] g(\text{MeOH}) \end{aligned} \quad (16)$$

$$\begin{aligned} \dot{g}(\text{MeOH}) &= \lambda_9(\text{MeOH}) y(\text{MeOH}) \\ &- \nu_9 \exp\left[-\frac{E_{\text{MeOH}}}{kT_d}\right] g(\text{MeOH}) \end{aligned} \quad (17)$$

where $g(\text{MeOH})$ is the fraction of MeOH molecules resident on grain surfaces, $G(\text{MeOH})$ is the right-hand side of equation (3) and $\nu_9 = 10^9 \nu_{\text{MeOH}} = 2.2 \times 10^{21} \text{s}^{-1}$ (Sandford & Allamandola 1993). The abundances of H_2O and Me_2O and HCOOH obey similar equations. The exact chemical composition at any T_d will depend crucially on the relative values of the binding energies, E_X adopted.

The recondensation theory implies several relations must hold. It is intuitively obvious that one requires $E_{\text{MeOH}} > E_{\text{Me}_2\text{O}}$. In both W3(H_2O) and G34.3 water evaporation has occurred, and each still exhibits high gas phase abundances (Table 1; Gensheimer et al. 1996) indicating that substantial H_2O recondensation has not occurred in either core. These observations therefore require $E_{\text{MeOH}} > E_{\text{H}_2\text{O}}$. Compared to their maximum (i.e. grain mantle) abundances of $\sim 10^{-7}$ and $\sim 10^{-6}$, formic acid appears to be more depleted than methanol in hot cores where the methanol abundance is only slightly less than its mantle value, probably due to destruction by gas phase reactions. If the inferred HCOOH depletion is in fact due to recondensation then we require $E_{\text{HCOOH}} > E_{\text{MeOH}}$. In total, the theory suggests the following hierarchy of binding energies

$$E_{\text{HCOOH}} > E_{\text{MeOH}} > E_{\text{H}_2\text{O}} \gg E_{\text{Me}_2\text{O}} \quad (18)$$

It should be emphasised that the conditions under which recondensation may occur in hot cores are different from those whereby gas species accrete on to dust in dark clouds. Apart from the higher gas and dust temperatures, the probable nature of the surface for sticking needs to be considered.

Early in the evolution of the cold gas that ultimately is incorporated in a hot core, molecular species accrete onto refractory grain cores of silicate, graphite and amorphous carbon, or conglomerations of these.

At 10K, atoms can be physisorbed and so a mantle of primarily H_2O molecules is first to form (e.g. Brown & Charnley 1990). The appropriate binding energies are those of molecules sticking to 10K surfaces of either mainly H_2O , or, to CO , O_2 and N_2 if a volatile crust surrounds the water molecules. In fact, astrochemical gas-grain models of cool, ultradense cores (Charnley 1997b) and protostellar disks (Charnley 1995; Aikawa et al. 1997) show that the binding energies needed to maintain a viable gas phase are close to those determined for physisorption between pure nonpolar or weakly-polar substances, e.g. CO on CO , consistent with the outermost layers comprising mostly of these molecules and not much H_2O . As the core heats up, reaching in excess of 100K, outgassing is controlled by these binding energies, i.e. those measured by Sandford & Allamandola (1993), and molecules are gradually evaporated according to their relative binding energies.

In hot cores, recondensation may occur at dust temperatures of about 90-100K and the appropriate surface for the initial sticking collisions will, according to (18), not be a water ice mantle. There are two possibilities: either bare silicate and/or graphite-amorphous carbon cores, or the organic residue surrounding these refractory cores after millions of years of ultraviolet photolysis and radiolysis in the molecular cloud (e.g. Allamandola et al. 1997; Moore & Hudson 1998). Hence, the values of E_X applicable may be quite dissimilar from those usually considered for cold molecular clouds.

The published data falls roughly into three categories. First, condensation temperatures derived from vapour pressure data for enthalpies for pure molecular gas undergoing transitions from the liquid or solid phase (Nagagawa 1980; Yamamoto, Nagagawa & Fukui 1983; Léger, Jura & Omont 1985). Physically, the adsorption enthalpy in this case should correspond to the surface binding energy for that on a pure crystal of like molecules. Second there are theoretical estimates of surface binding/adsorption energies for molecules X on a silicate surface (Allen & Robinson 1977; Hasegawa & Herbst 1993). Finally, there are direct measurements of E_X from temperature-programmed ice desorption experiments (e.g. Sandford & Allamandola 1993).

Physisorption involves weak van der Waals-London bonding and E_X depends on the polarizability of the adsorbed species, α_X , and the composition of the surface, S , through the polarizability of the surface

atoms. One finds $E_X \propto \alpha_X \alpha_S$ (Masel 1996). Table 2 summarises the relevant theoretical and experimental data on binding energies, as well as some relevant molecular polarizabilities. It is clear that the theoretical binding energies do not reproduce the desired inequalities of (18) and in fact would predict that Me_2O should be the most susceptible to recondensation.

These theoretical values are also at variance with the experimental results. The E_X for adsorption on silicates, listed by Allen & Robinson (1977) and Hasegawa & Herbst (1993), are extrapolated from studies of hydrogen adsorption graphite. London's theory is successful in predicting physisorption energies for nonpolar molecules on nonmetallic surfaces, such as CO_2 on graphite, but extensions of the theory to polar molecules are generally less successful (Masel 1996). Table 2 shows that for CO_2 the theoretical and experimental values are in accord. However, this is not the case for H_2O adsorption where there is a large discrepancy. Such a low $E_{\text{H}_2\text{O}}$ could not reproduce the H_2O ice column density observed in the envelopes of OH/IR stars, environments where water molecules are actually condensing on to warm, bare, silicate grains; in this case one requires $E_{\text{H}_2\text{O}} > 4000\text{K}$ (Meyer et al. 1998).

The presence of the -OH group on each of the molecules of interest point to the importance of hydrogen bonding in determining the E_X . The strengths of hydrogen bonds are typically $10\text{--}40\text{ kJ mol}^{-1}$, compared to a few kJ mol^{-1} for van der Waals bonding. This is the reason why the experimental values for water and methanol are so much larger than the theoretical ones (cf. Table 2). The importance of hydrogen bonding in this context was noted by Léger et al. (1985). Neglect of hydrogen bonding is the reason why the theoretical binding energies closely track the molecular polarizabilities.

For hydrogen bonding of HCOOH and MeOH to occur, other OH-containing molecules must already be present on the grain surface. There are two cases of interest. First, bare silicate grains may have a surface structure similar to silanol with regularly spaced Si-OH groups available for hydrogen bonding (Tielens & Allamandola 1987). As the surface will be damaged, the occurrence of OH groups will be random in practice, and some of the Si atoms could also be replaced by others in the solid (e.g. Fe and Mg). The actual adsorption potential at any point on the surface may depend on the proximity of a hydroxyl group with a contribution from the polarizability of

adjacent species. The relative polarizabilities are indeed in the desired ordering (cf. equation 18)

$$\alpha_{\text{HCOOH}} > \alpha_{\text{MeOH}} > \alpha_{\text{H}_2\text{O}} \quad (19)$$

Second, an organic residue containing OH groups could be present. The ices in hot cores are rich in aliphatic alcohols prior to evaporation (Charnley et al. 1995; Charnley 1999a). If high molecular weight alcohols are not desorbed significantly when $T_d > 100\text{K}$, then they might provide the necessary binding sites. Apart from hydrogen bonding amongst themselves, these compounds have larger polarizabilities and so are not easily sublimed. Support for this picture comes from the experiments of Bernstein et al. (1995) who found that EtOH was retained at 150–200K, after H_2O and CH_3OH had evaporated, in the organic residue that persisted at the end-point of UV-photolysis and heating. This implies $E_{\text{EtOH}} > E_{\text{MeOH}}$ and suggests that the low ethanol abundance seen in most hot cores could also be due to recondensation. The random occurrence of surface hydroxyls and the α_X distribution probably also influence the surface potential, as remarked above. It is perhaps worth noting that the strength of the hydrogen bond amongst carboxylic acids is stronger than amongst alcohols, and both are stronger than water (Pauling 1940). If this trend carries over for binding to arbitrary surface OH groups, then it would also reproduce the desired E_X ordering.

5. A Numerical Model

This effect can easily be demonstrated in hot core models and here a calculation is presented to illustrate the ideas of the preceding sections. For constant ion fractions, equation (6) is an Abel equation of the second kind and although it is possible to solve many aspects of the chemistry analytically (Charnley 1999b), this is generally not possible when T_d is a function of time, $T_d(t)$. The results presented here were therefore obtained using a numerical model.

5.1. Astronomical Binding Energies

We need to estimate what numerical values of E_X are inferred by the observations. We assume that all the H_2O , CH_3OH and HCOOH present in either gas or ice originated in grain surface chemistry. The total abundance of molecule X in a core is then

$$Y(X) = y(X) + g(X) \quad (20)$$

Unfortunately the ice inventory towards each of the three sources in Table 1 is not known but we can take ‘canonical’ values for the $Y(X)$ as measured in other sources. Relative to molecular hydrogen (i.e. $2y(X)$ etc.), for H_2O , MeOH , and HCOOH these are 5×10^{-5} , 1×10^{-6} and 2×10^{-7} , respectively (Gensheimer et al. 1996; Blake et al. 1987; Menten et al. 1988; Schutte et al. 1996). Ignoring gas phase chemistry, we can balance accretion and desorption rates to get

$$E_X = T_d \ln \left[2.2 \times 10^{17} \left(\frac{M_X}{T} \right)^{0.5} \frac{\nu_X}{n_{\text{H}}} \left(\frac{Y(X)}{y(X)} - 1 \right) \right] \quad (21)$$

The actual dust temperatures are also not accurately known but T sets an upper limit. Adopting $T_d = 100\text{K}$, using ν_X from Sandford & Allamandola (1993), and the values for G34.3 in Table 1, we find $E_{\text{H}_2\text{O}} = 5171\text{ K}$. Using this binding energy and the parameters of $\text{W3(H}_2\text{O)}$ gives $T_d = 95\text{K}$, again in good agreement, and so we adopt the above value for $E_{\text{H}_2\text{O}}$. This is in excellent agreement with the measured value for annealed H_2O (Table 2) and is consistent with the grains being gradually heated and annealed prior to evaporation with any recondensation yielding crystalline ice. Indeed, the $3\mu\text{m}$ water ice absorption spectrum of the BN object in Orion does show evidence for a crystalline component (Smith et al. 1989).

Assuming 95K dust in $\text{W3(H}_2\text{O)}$ leads to $E_{\text{MeOH}} = 5264\text{ K}$. In G34.3, with 100K dust, E_{MeOH} is estimated to be in the range 5295–5410 K, depending on which methanol abundance in Table 1 is used. We adopt $E_{\text{MeOH}} = 5270\text{ K}$ as a representative value. This range is higher than published methanol physisorption energies. For comparison, Sandford & Allamandola give $E_{\text{MeOH}} = 4240\text{K}$ for pure methanol; this could not explain the $\text{W3(H}_2\text{O)}$ MeOH abundance if $T_d \approx 95\text{K}$. Similarly, the theoretical value of $E_{\text{MeOH}} = 2060\text{K}$ requires $T_d \approx 38\text{K}$ - too low for $\text{W3(H}_2\text{O)}$ and predicts large methanol enhancements in cool cores which are not observed, e.g. at 55K in W3(IRS5) (Helmich and van Dishoeck 1997).

Experimental measurements for E_{HCOOH} are not available. Based on the trend of condensation temperatures of the pure substances (Nakagawa 1980) a relatively large value might be expected, much larger than the theoretical value of 2570K in Table 2. With a frequency factor of $2 \times 10^{12}\text{s}^{-1}$, 100K dust, and an inferred gas:solid ratio of 100:1 in G34.3, equation

(20) yields $E_{\text{HCOOH}}=5867$ K.

Dimethyl ether will not participate in hydrogen bonding and the value of 2820 K given by Hasegawa & Herbst (1993) is probably appropriate.

It should be emphasised that these estimates depend on the unknown ice abundances in these particular cores. Note that the estimated E_{HCOOH} and E_{MeOH} are for binding to the hypothetical OH-containing surface, silanol or organic residue, whereas once a water ice monolayer has formed $E_{\text{H}_2\text{O}}$ and the remaining E_X will be determined by their interaction with surface water molecules.

5.2. Model

The numerical model is that used by Charnley (1997a) except that the rate coefficients were updated from Millar et al. (1997) and the differential equations for H_2O , MeOH , HCOOH , Me_2O and all other neutral molecules were modified in line with equations (16) & (17), and including the binding energies of §5.1. Starting from an initial gas phase at 10K, comprising only of H_2 , He, H and their related ions, the dust temperature is raised to about 150K and the mantles are evaporated. It is assumed that no refractory metals are present (see Charnley 1997b). The abundances (i.e. $y(X)$) of H_2O , CO, MeOH, and HCOOH injected were taken from §5.1. The core has a density of $n_{\text{H}} = 2 \times 10^6 \text{ cm}^{-3}$, the visual extinction was taken to be 300 magnitudes, the cosmic ray ionization rate was taken to be $1.3 \times 10^{-17} \text{ s}^{-1}$. The effects of cosmic ray-induced photochemistry were ignored.

Based on the binding energies of §5.1, it is assumed that the grains cool to where CH_3OH and other molecules can recondense but that they remain hot enough that more volatile species, such as ethers, do not. To keep the model as simple as possible, a simple grain cooling law was adopted

$$T_d(t) = 150 \exp(-t/\tau_{\text{cool}}) \quad (22)$$

and calculate the core chemistry for various values of τ_{cool} . In fact, τ_{cool} is relatively well constrained by the requirements that it be less than the dynamical life-time of the core, about 2×10^5 years, but also be long enough for the CH_3OCH_3 abundance to grow to its observed value. To produce $\text{CH}_3\text{OCH}_3/\text{H}_2$ abundances of $\sim 10^{-8}$ for an injected $\text{CH}_3\text{OH}/\text{H}_2$ fraction of 10^{-6} places a lower bound on τ_{cool} of around 5000-10,000 years (Charnley et al. 1995). In summary, the

calculation proceeds with the dust instantaneously heated to 150K, as in previous hot core models, it is then allowed to cool to 100K on a time-scale of τ_{cool} where it is held fixed for 2×10^5 years. Calculations are presented for τ_{cool} equal to 10^4 years, as well as for the case $\tau_{\text{cool}} = \infty$ to account for the case of no recondensation, as assumed in all previous work.

The models shown in Figure 1, where the calculated abundances are presented as relative to molecular hydrogen (i.e. $2y(X)$), show that the recondensation scenario can be realised in hot core models and that it has a dramatic effect on the core composition. It is suggested that this process is occurring to some extent in G34.3 and W3(H_2O).

6. Conclusions & Discussion

Early in the lives of embedded massive protostars, a slight reduction in the protostellar luminosity causes the local dust temperature to fall and permits recondensation of molecules that were evaporated previously when the dust was warmer. Such a scenario can explain the apparently anomalous abundances of methanol and its daughter molecules CH_3OCH_3 and HCOOCH_3 in G34.3 and W3(H_2O), as well as the low abundances of HCOOH, and perhaps also EtOH, generally seen in hot cores.

Hydrogen bonding must be important in determining the binding energies of molecules containing the hydroxyl group and the appropriate values have been derived from the astronomical observations. This work suggests that it may be possible to determine molecule-grain binding energies for many species. If the physical conditions along particular sightline are well known, especially the dust temperature in the hot core component, then, for molecules produced on grains, the gas:solid abundance ratio will allow an estimate of E_X to be made and depletions predicted for other cores. In practice one must be cautious since one is dealing with spatial gradients in density and temperature and so estimating values may not be as straightforward as presented here.

One consequence of this theory is that the entire composition of interstellar ices will only be present in gas at 150K or more. The fact that many complex products of grain surface chemistry (e.g. alcohols) contain O-H and N-H bonds means that they will form hydrogen bonds with either a silanol-like surface, or organic residue, and consequently will have large binding energies. The fact that, relative to water, the

abundances of HCOOH , NH_2CHO and HNCO in hot cores are significantly depleted with respect to those seen in the coma of Comet Hale-Bopp (see Crovisier 1998) suggests that recondensation may be occurring in the former sources.

Finally, molecular recondensation may also occur around low-mass protostars, either following mantle removal in shock waves or, in more evolved objects, as a result of FU Ori outbursts. The latter case will be discussed elsewhere and we note here that Avery and Chiou (1996) have already identified recondensation of CH_3OH and SiO as a possible explanation for the peculiar chemical abundances observed in the L1157 bipolar outflow.

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TABLE 1
OBSERVED ABUNDANCES IN HOT CORES

Molecule	Compact ^a Ridge	W3(H ₂ O) ^b	G34.3 ^c
H ₂ O ^d	5000 [†]	770	4300
CH ₃ OH	94.0	4.6	10.0/3.4
CH ₃ OCH ₃	4.7	1.0	1.0/-
HCOOCH ₃	7.8	0.3	1.0/3.0
HCOOH	0.3	-	-/0.2
T_{gas} (K)	70-150 ^e	100	75-190 ^f
n_{H} (10 ⁶ cm ⁻³)	> 1 ^e	~5	1 ^f

Entries are fractional abundances relative to H₂ divided by 10⁻⁸. Dust and gas are assumed to have equal temperatures.

^a Sutton et al. (1995); calculated using CO/H₂=2.7×10⁻⁴ (Helmich & van Dishoeck 1997)

^b Helmich & van Dishoeck (1997)

^c For G34.3, two values are given: Mehringer & Snyder (1996)/MacDonald et al. (1996)

^d Gensheimer et al. (1996)

^e Blake et al. (1987)

^f Millar et al. (1997b) for the 'compact core'. The 'ultra-compact core' has $T_{\text{gas}} \sim 300\text{K}$

[†] Not detected specifically in the Compact Ridge; estimate based on HDO/H₂=10⁻⁸ and HDO/H₂O=2×10⁻⁴

TABLE 2
BINDING ENERGY DATA

X	X-SiO ₂ ^a (K)	X-H ₂ O ^b (K)	X-X ^b (K)	α_X^c (10 ⁻²⁴ cm ³)
CH ₃ OCH ₃	2820	-	-	5.29
H ₂ O	1860	4815 [†]	4815 [†]	1.45
		5070 [‡]	5070 [‡]	
CH ₃ OH	2060	-	4235	3.29
HCOOH	2570	-	-	4.42
CO	1210	1740	960	1.98
NH ₃	1110	-	3075	2.26
EtOH	3470	-	-	5.41
CO ₂	2500	2860	2690	2.63

Binding energies denoted X-S are for adsorption of molecule X on surface S. α is the polarizability.

^a Hasegawa & Herbst (1993) and Allen & Robinson (1977); theory.

^b Sandford & Allamandola (1993); experiment.

^c Gonzalez et al. (1997) and Miller (1997); experiment and theory.

[†] unannealed ice.

[‡] annealed ice.

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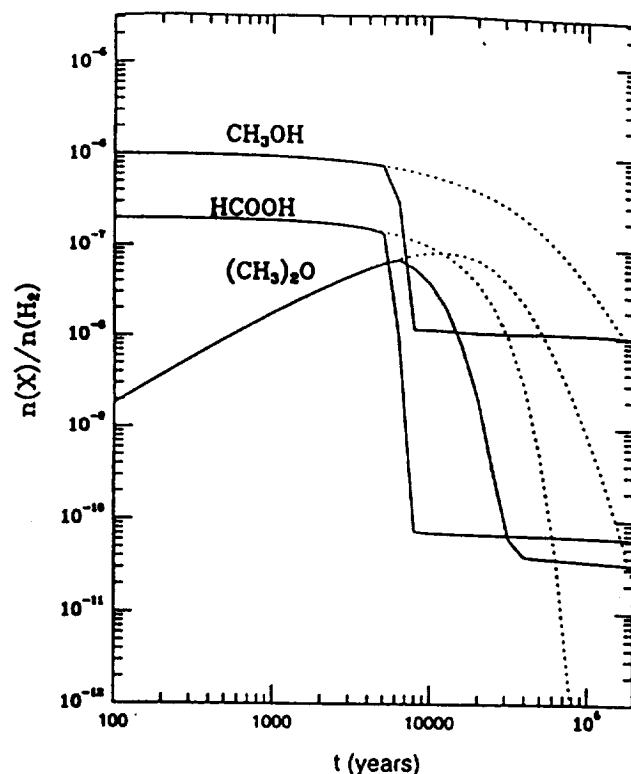


Fig. 1.— Chemical evolution in a hot core where molecules are recondensing on to cooling dust grains (full lines) and where no recondensation occurs (broken lines). See text for details.